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Conversion of Alkoxide Solutions to Oxides: Evaporation of Products

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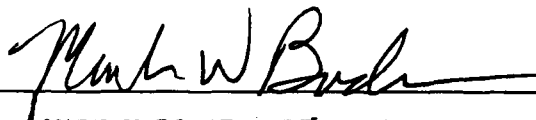
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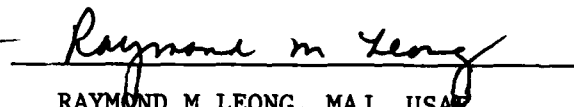
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<p>The evaporation of organic by-products released during drying of 1-mm thick silicon tetramethoxide gels was analyzed using gas chromatography. The evaporation kinetics of methanol depended on the drying rate achieved by flowing dry air over the gel. For drying at flow rates less than 50 cm³/min, exponential kinetics were observed initially with a long time constant (about 100 to 400 min). For drying rates greater than 70 cm³/min, diffusional (t^{-1/2}) kinetics were observed initially. Cracking of the gel during drying was used to indicate the degree of stress. At low drying rates, minor cracking was observed near the edges of the gel. At high flow rates, extensive cracking was observed in samples that exhibited early t^{-1/2} kinetics. Monitoring the kinetics of drying is essential to optimizing the drying conditions to minimize stress and cracking in gels.</p>					
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PREFACE

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I. INTRODUCTION

The rate of solvent and organic by-product removal from wet gels prepared by metallo-organic solution deposition (MOSD or sol-gel) affects the structure and quality of the dry gels and films.¹⁻³ At slow drying rates, evaporation of solvent from the gel depends on the vapor pressure of the solvent, its surface concentration, and its surface area.⁴ When the surface dries faster than the solvent can diffuse to the surface, transport of the solvent molecules to the surface becomes rate limiting. Drying conditions are usually optimized by the traditional method of examining dried gels or films and adjusting the drying conditions to avoid cracking. An understanding of evaporation kinetics would result in easier optimization of drying conditions. Thermogravimetry (TG) could be used to monitor the evaporation kinetics. However, in multicomponent solvent systems, measurement of the evaporation of the individual components is desirable, which is possible by gas chromatography. In this report, we show that gas chromatography can be used to characterize drying kinetics of gels. Tetramethylorthosilicate (TMOS) was studied as a model system to demonstrate the application of this technique. The rate of dry air flow was used to vary the drying rate over a wide range, and the observed evaporation kinetics were correlated to cracking in the dried gel.

II. EXPERIMENTAL PROCEDURE

The gels were cast from solutions with mole ratios of TMOS:water:methanol:ammonium hydroxide of 1:4:4:0.13. Distilled TMOS, reagent grade methanol, and aqueous ammonium hydroxide were used. Gelation occurred after 2 hr at 24°C. The gel was aged for an additional hour prior to drying measurements.

The drying experiments were carried out in a 2-ml volume sample tube containing a 1-mm thick wet gel cast into a 1-cm x 2-cm area. The drying rate was controlled by flowing dry air into the sample tube at rates between 11 and 105 cm³/min. The gas exiting the tube through a 3-mm diameter capillary was sampled at 1- to 20-min time intervals by an automatic 6-port gas sampling valve. The concentration of methanol vapor in 2-ml gas samples was determined with an HP 5480A gas chromatograph equipped with an Alitech AT-1000/Graphpac column. The column was run at 160°C, the nitrogen carrier flow was set at 25 cm³/min, and a flame ionization detector was used. The peak intensity was related to the vapor pressure of methanol by running methanol in the cell under the same conditions as the gels.

III. RESULTS AND DISCUSSION

The primary species observed by gas chromatography during drying in air at 24°C were methanol and TMOS monomer. (Water cannot be detected using a flame ionization detector.) A sequence of gas chromatograms obtained by sampling the gas exiting the flow cell at 20-min intervals is presented in Figure 1. The evaporation rates of methanol and TMOS are compiled in Table 1.

The high degree of polymerization and lower monomer volatility accounts for the very low TMOS evaporation rate. Most of the volume change of the gel is due to the evaporation of methanol. The evaporation kinetics, which were investigated in detail, were related to cracking of the gel.

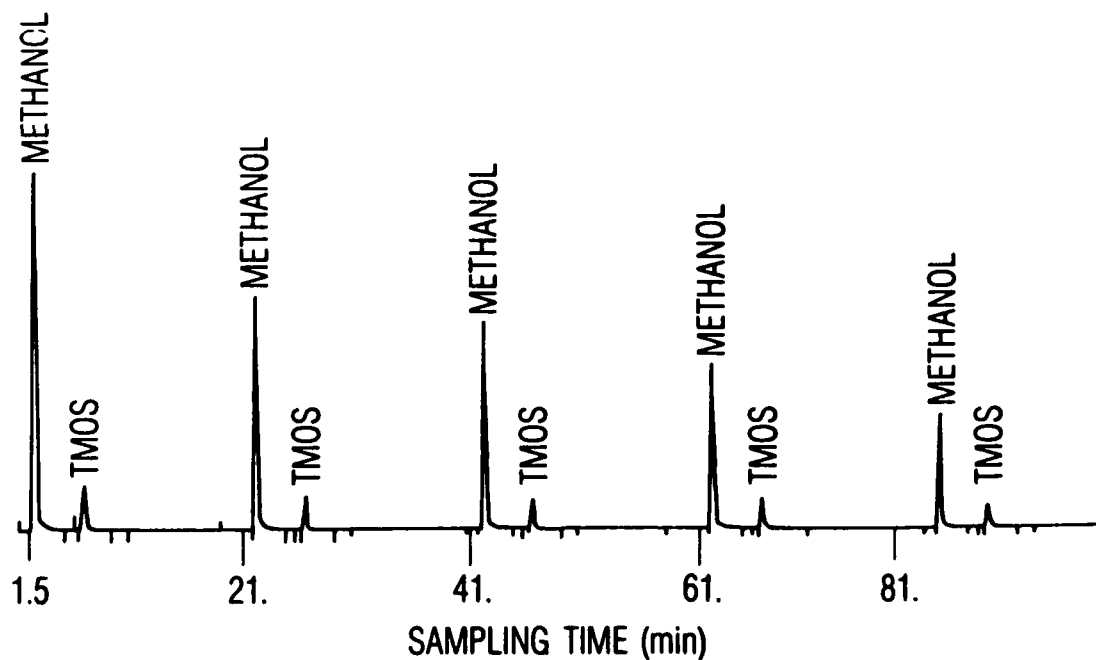


Figure 1. Gas Chromatograph of TMOS Sample (carrier flow=35 cm³/min)

Table 1. Gas Chromatography of Gases Removed from
Base-Catalyzed TMOS Gel by Dry Air
Flowing at 35 cm³/min

Sampling time (min)	Observed time (min)	Compound	Evaporation rate (μmoles/min cm ²)
1.5	2.0	methanol	35.0
	6.4	TMOS	1.3
21.0	21.5	methanol	23.0
	25.9	TMOS	0.8
41.0	41.5	methanol	20.0
	45.8	TMOS	0.9
61.0	61.5	methanol	8.0
	65.8	TMOS	0.9
81.0	81.5	methanol	11.0
	85.8	TMOS	0.7

The flow rate through the cell was varied between 11 to 105 cm³/min to measure its effect on the drying rate of the gel. The evaporation kinetics of methanol from the TMOS gels at three different air flow rates are compared in Figures 2 and 3. The data in Figure 2 for moderate flow rates (11 and 35 cm³/min) indicate two distinct regions: an initial region (until about 80% of the methanol is lost) where the evaporation rate is fairly constant, and a region where the rates abruptly decrease. These regions are referred to in the ceramics literature, respectively, as the "constant rate period" and the "transition period."⁵ The evaporation kinetics in the constant rate period shown in Figure 3 can be fitted by

$$dN/dt = E_0 \exp(-t/t_0) \quad (1)$$

where E_0 is the initial evaporation rate and t_0 is the time constant. These parameters are tabulated for several flow rates in Table 2.

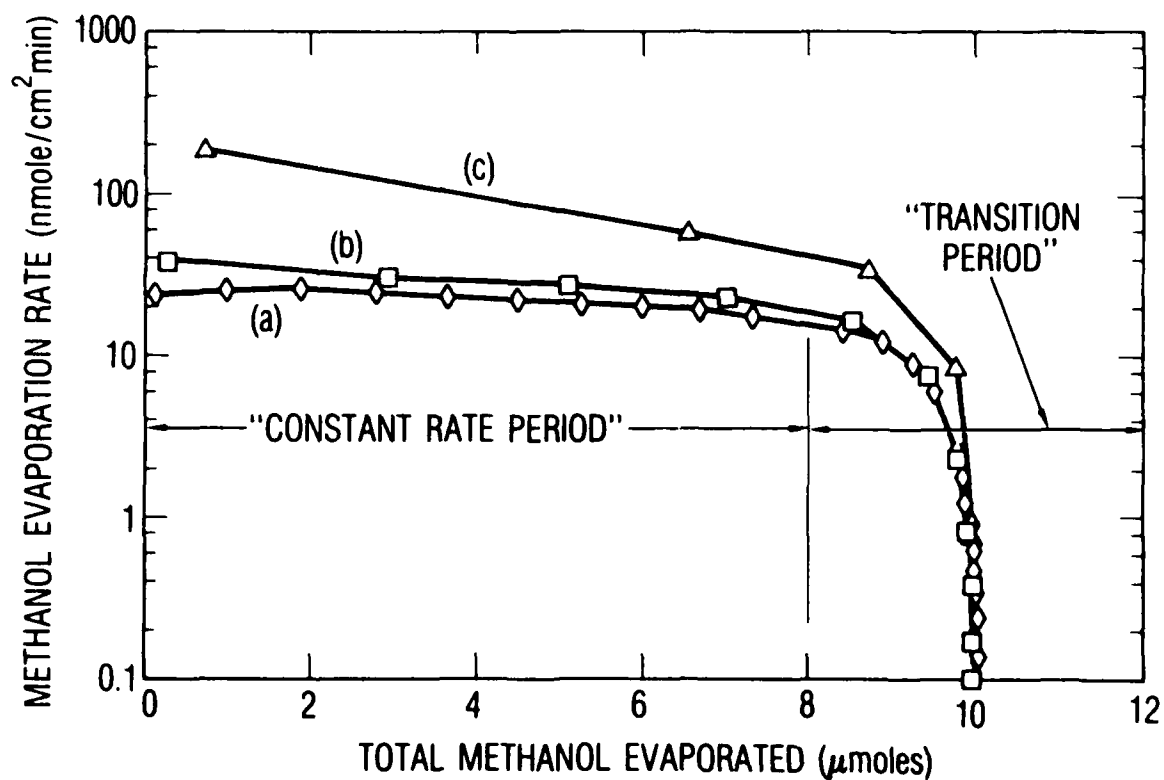


Figure 2. Evaporation Rate of Methanol from TMOS Gels at 24°C for Flow Rates of (a) 11 cm³/min, (b) 19 cm³/min, and (c) 105 cm³/min

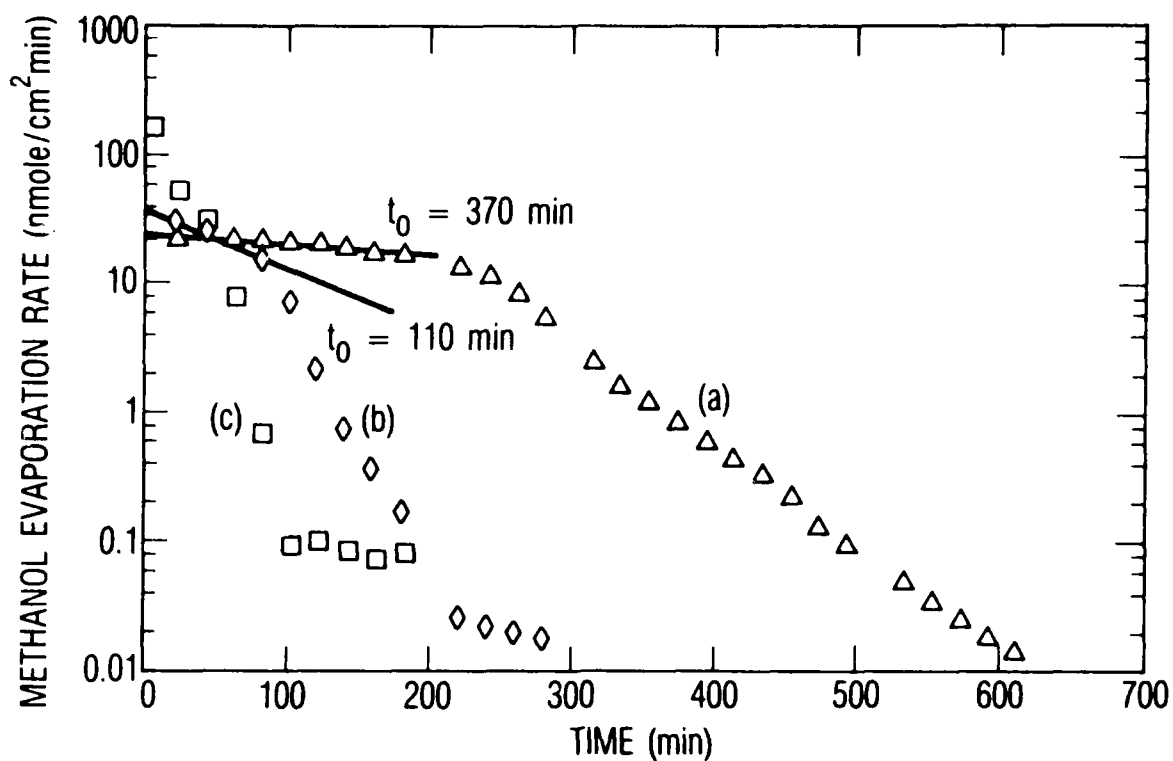


Figure 3. Evaporation Rate of Methanol from TMOS Gels at 24°C for Flow Rates of (a) 11 cm³/min, (b) 19 cm³/min Showing Exponential Fit to Initial Data, and (c) 105 cm³/min.

Table 2. Effect of Air Flow Rate on Drying

Air Flow, f (cm ³ /min)	E_o (nmole/min cm ²)	t_o (min)	VE_o/f (nmole/min cm ²)	ft_o/V
11	8	370	1.5	2000
19	12	210	1.2	2000
35	17	110	1.0	1900
72	$t^{-0.42}$		-	-
105	$t^{-0.51}$		-	-

To understand the observed kinetics, a simple model of drying was proposed (as shown in Figure 4). At low rates of air flow, the surface of the gel remains wet as the gel collapses.⁶ Assuming ideal solution behavior for methanol in the gel, the surface concentration of methanol available for evaporation is nearly proportional to the concentration of methanol remaining in the gel. Under this assumption, the equations for the rate of change of methanol in the vapor phase, dN_v/dt , and in the gel phase, dN_g/dt , are the same as those for outgassing:⁷

$$dN_v/dt = k_v N_g - k_c N_v - f N_v/V \quad (2)$$

$$dN_g/dt = -k_v N_g + k_c N_v \quad (3)$$

where k_v is the vaporization rate of methanol from the surface, k_c is the condensation rate, f is the gas flow rate, N_g is the number of moles of methanol in the gel, V is the volume of gas sampled by the gas chromatograph, and N_v is the number of moles of methanol in the vapor phase in the cell. The quantity measured by sampling the gas at the exit of the sample cell is dN_v/dt . At a constant air flow rate, a steady state is established in the vapor phase and dN_v/dt in Eq. (2) can be set equal to zero. Under these conditions, the solutions of Eqs. (2) and (3) are

$$N_g(t) = (k_c/k_v) N_{eq} \exp[-k_v f t / (V k_c + f)] \quad (4)$$

$$N_v(t) = [k_c / (k_c + f/V)] N_{eq} \exp[-k_v f t / (V k_c + f)] \quad (5)$$

where N_{eq}/V is the equilibrium concentration of methanol with no air flow. The evaporation rate measured by the gas chromatograph was calculated from Eq. (5) and is:

$$dN_v(t)/dt = [k_c / (k_c + f/V)] [k_v f / (V k_c + f)] N_{eq} \exp[-k_v f t / (V k_c + f)] \quad (6)$$

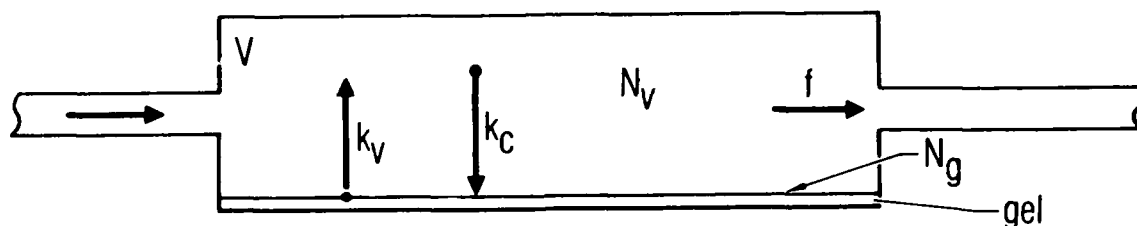


Figure 4. Kinetic Model for Drying of Gels in Flowing Air

Assuming low to moderate flow rates ($f/V \ll k_C$), E_0 and t_0 can be related to the kinetic parameters of the model by comparing Eq. (6) to Eq. (1). The initial evaporation rate is given by

$$E_0 = (k_V f / V k_C) N_{eq} \quad (7)$$

and the time constant is given by

$$t_0 = V k_C / k_V f \quad (8)$$

As predicted from the model, VE_0/f and ft_0/V calculated from the data in Table 2 are constant within the experimental uncertainty. Thus, for flow rates less than $35 \text{ cm}^3/\text{min}$, the observed exponential drying kinetics are consistent with evaporation of methanol of an ideal solution consisting of methanol and nonvolatile gel. The stress on the gel is low under these conditions.⁶

At high air flow rates, the initial kinetics change to a $t^{-1/2}$ law. This is shown for the data in Figure 5, obtained with a flow rate of $105 \text{ cm}^3/\text{min}$. The $t^{-1/2}$ law is expected for plane diffusion from an infinitely thick plate.⁷ These conditions exist for a limited time in a rapidly drying gel when solvent is removed more rapidly than a gel can contract or the liquid can flow. Based on our observations, drying under these conditions seriously increases the cracking in the gel.

Cracking of the 1-mm thick gels did not significantly change the surface area of the gels or change the measured drying rates. At flow

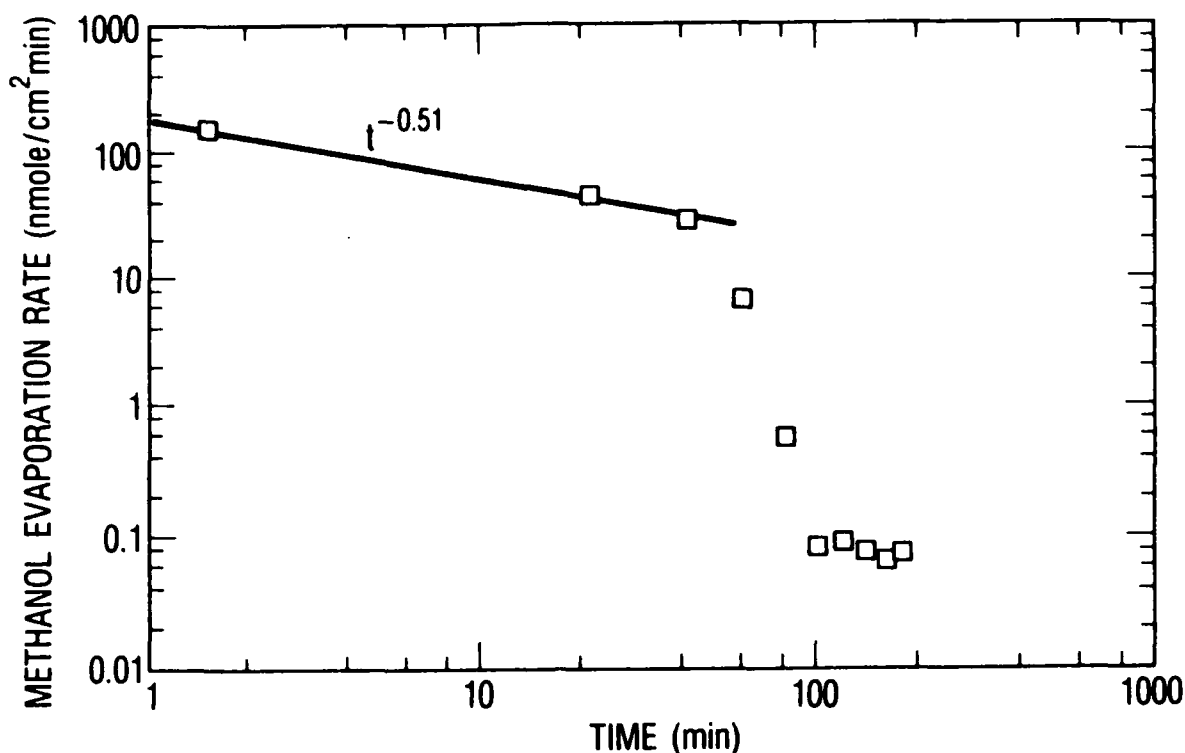


Figure 5. Evaporation of the Methanol at a High ($105 \text{ cm}^3/\text{min}$) Flow Rate

rates less than $35 \text{ cm}^3/\text{min}$, minor cracking developed along the edges of the gel after about 20% of the methanol was removed (Figure 6). Further drying caused the gel to shrink, but no additional cracks developed. At flow rates greater than $70 \text{ cm}^3/\text{min}$, extensive cracking occurred before 10% of the methanol was removed. The type of cracking typical of rapid drying and diffusion-limited kinetics is shown in Figure 6b. Further cracking occurred as the gel shrank during additional drying.

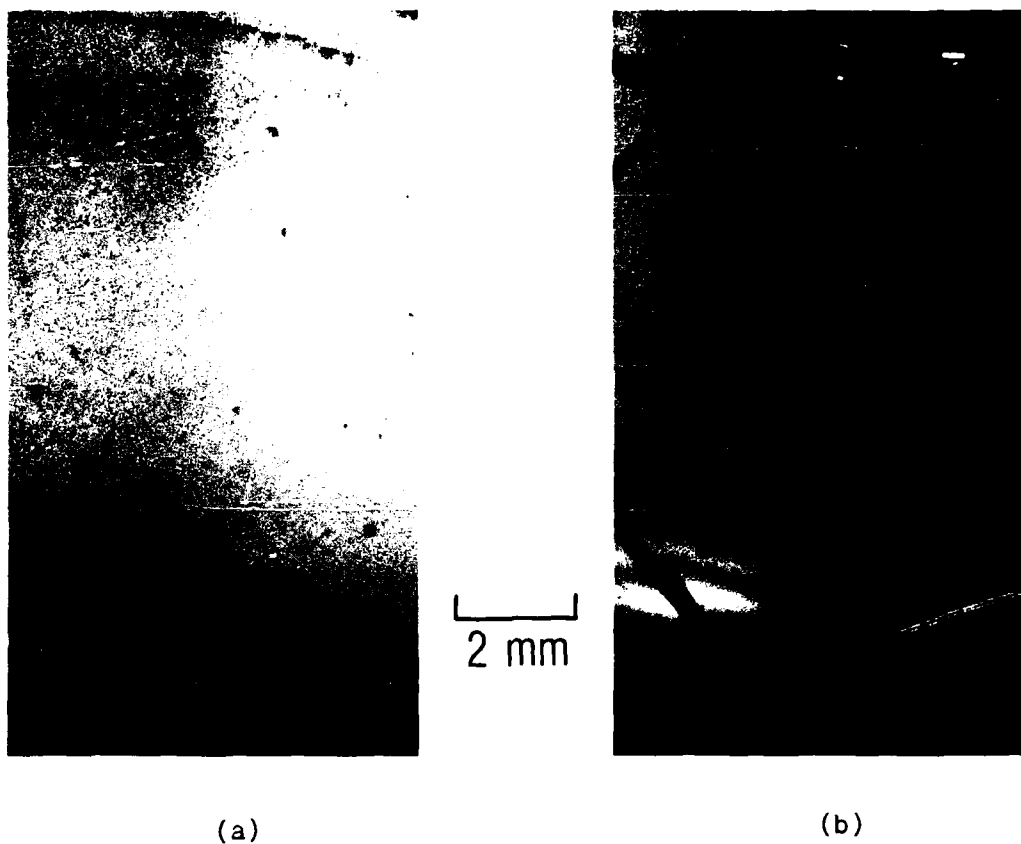


Figure 6. Cracking in Gels Dried at (a) $19 \text{ cm}^3/\text{min}$ to Remove 20% of the Methanol and (b) $105 \text{ cm}^3/\text{min}$ to Remove 25% of the Methanol

IV. CONCLUSIONS

Evaporation kinetics over a wide range of air flow rates (11 to 105 cm³/min) were measured using gas chromatography and were correlated to the cracking of the gels. Cracking in TMOS gels was minimized when the rate of methanol evaporation followed exponential kinetics and the gel dried uniformly. Extensive cracking was observed when the methanol evaporation followed diffusion-limited kinetics. Using this correlation between kinetics and cracking, gas chromatography can be used to measure the kinetics and optimize the drying rate of wet gels. This technique will be particularly useful in understanding the effects of evaporation in mixed solvent systems.

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